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The Method for Investigating the Structurization of Water-Organic Mixtures

S Karitskaya

Ural Federal University named after first President of Russia B.N. Eltsin, Yekaterinburg, Russia

E-mail: sv.karitskaya@rambler.ru

Abstract. The investigation of the properties of micellar systems is of great practical importance, since the microheterogeneous structure, in particular, of aqueous-organic solutions can be used to create reaction centers with designed properties, which will make it possible to increase the efficiency of processes associated with the intramolecular conversion of the electronic excitation energy of a molecule. In the present paper, model systems to stimulate chemical reactions are the spatial-temporal structures (STS) formed as a result of photophysical and photochemical reactions, whose time characteristics are highly sensitive to a change in the solvent compositions. The STS evolution processes are slow and the structures formed have macroscopic sizes, which makes the system under consideration a convenient object for experimental studies. The spectral and time characteristics of the spatial-temporal structures luminescing when exposed to UV radiation in aqueous alcohol solutions of anthraquinone are investigated experimentally depending on the volume content of alcohol in a mixture. It is shown that the microheterogeneous structure of aqueous alcohol solutions considerably influences the behavior of the dissipative structures formed.

1. Introduction

The effect of the appearance of self-organization in open systems – the formation of the so-called "dissipative" structures – has found widespread application in various fields of physics, chemistry, biology, and medicine. Such structures make it possible to model processes in cells and tissues, investigate the influence of physical fields on chemical processes, and elaborate new methods of information recording, storage, and transformation.

It has been found that the appearance of an STS is a general property of air-saturated solutions of organic chromophores in organic solvents when photochemical reactions initiated by UV radiation proceed in them. In the systems considered, with an initially uniform reaction-volume distribution of original substances, space- and time-inhomogeneous photophysical and photochemical reactions leading in the final analysis to the formation of STSs proceed. The STS evolution is characterized by an induction period, after which the initially volume-uniform distribution of concentrations of reagents and products changes stepwise into an inhomogeneous one.

Previously [1], the phenomenon of heat-and-mass transfer in the form of redistribution of concentrations of reagents and photoreaction products in the reaction-space volume in alcohol solutions of anthraquinone at various ketone concentrations was investigated. It was shown that the luminescent photoproduct (ketyl radical) of anthraquinone [1-3] is responsible for the formation of structures in this system. The STS evolution processes are slow and the structures formed have

macroscopic sizes, which makes the system under consideration a convenient object for experimental studies.

2. Results and Discussion

Anthraquinone is classified as substance with the quantum yield of fluorescence close to zero [3]. As diketone, anthraquinone is subject to reaction of photodehydrogenation by spirit. A yellow coloring and green fluorescence, which are attributed its long living ketyl radical, it is observed at UV irradiation an alcohol solution of anthraquinone [2].

It has been shown by experiment [1] that the formation of luminescent ketyl radicals proceeds with the highest efficiency by the mechanism of anthraquinone in solvents — hydrogen atom donors:

$$^3A_1 + RCH_2OH \xrightarrow{k = 3 \cdot 10^6 M^{-1} \cdot \sec^{-1}} AH^{\bullet} + RCHOH^{\bullet}$$

where $^3A_1$ and $AH^{\bullet}$ are, respectively, the triplet state of the molecule and the anthraquinone radical and RCH_2OH and $RCHOH^{\bullet}$ are the alcohol molecule and the radical, respectively.

The ketyl radical is formed after some induction period after the beginning of irradiation. The induction period depends on such factors as: anthraquinone concentration, oxygen concentration, laser radiation intensity, temperature and a thickness of an irradiated layer [1]. It is known that the rate constant of the reaction of formation of a luminescent photoproduct of anthraquinone is $3 \cdot 10^6$ liters/mole·sec [2], which is three orders of magnitude less than the diffusion rate constant. Therefore, for the formation of a luminescent photoproduct of anthraquinone to be successful it is essential that the partners in the reaction stay at the "reaction" distance from one another for a fairly long time. This condition is satisfied by the dynamic characteristics of the boundary-layer molecules. The experiment has revealed that luminescent regions appear in the first place at glass–solution or air–solution interfaces (provided the laser beam is directed perpendicular to the cell base.

It is known that at certain concentrations of surface-active substances in the solvent micelles — elementary heterogeneous liquid structures — are formed. The investigation of the influence of the medium micro heterogeneity providing a considerable area of the interface is of interest.

Alcohol is known to be a good donor of hydrogen. At the same time, alcohol, like the majority of organic compounds, is surface-active with respect to water [4]. This means that the structure of water-alcohol solutions will differ from the structure of pure alcohol solutions (due to the micelle formation). As a consequence of this, the total area of the alcohol–water interface becomes fairly large. Since, as mentioned above, the interface plays an important role in the STS development, it would be expected that the microheterogeneous structure of water–alcohol solutions will change the rate of intermolecular energy transfer and will thus influence the process of anthraquinone photoproduct formation and, consequently, the appearance of an STS. Therefore, one promising method for controlling energy phototransformations in the system under consideration is the use, as a solvent, of a water–alcohol mixture, which, on the one hand, is a hydrogen atom donor and, on the other hand, (due to the microheterogeneity of its structure caused by the presence of a density gradient at the interface) exhibits properties radically differing from the properties of homogeneous media and true solutions.

Anthraquinone, which is the basis of a variety of synthesized dyes, has an extremely low solubility in water [5]. Anthraquinone molecule from a position of the molecular dynamics method is a classic example of heterofunctional molecule with a large hydrophobic surface formed by >CH-groups of aromatic rings, and hydrophilic centers - oxygen atoms.

Analysis of the obtained spectral characteristics of the solutions under investigation has shown that the shape of the absorption and luminescence spectra and the positions of the absorption and luminescence maxima of the alcoholic and water-alcohol solutions of anthraquinone of various concentrations are analogous. This indicates that in the water–alcohol solutions of anthraquinone, independent of the mass concentration of alcohol, the ketyl radical is responsible for the luminescence.

A change in the mass content of alcohol in the water–alcohol mixture produces a strong effect on the time characteristics of different stages of STS evolution. For instance, the development of UV-

radiation-initiated structures in water-alcohol solutions of anthraquinone (at $C_A = 10^{-3}$ mole/liter) proceeds without the vibrational stage characteristic of alcoholic solutions and leads to the formation of a continuous luminescent zone along the whole laser-beam path 1–12 min after the irradiation of the solution depending on the alcohol concentration in the water–alcohol mixture (Figure 1). The STS evolution in water–alcohol solutions of anthraquinone with $C_A = 10^{-4}$ mole/liter is analogous evolution for alcoholic solutions but with smaller values of the time characteristics. The formation of a continuous luminescent zone for the given concentration of anthraquinone is observed after the third, "vibrational", stage of the STS evolution (later 3 hours of a continuous irradiation).

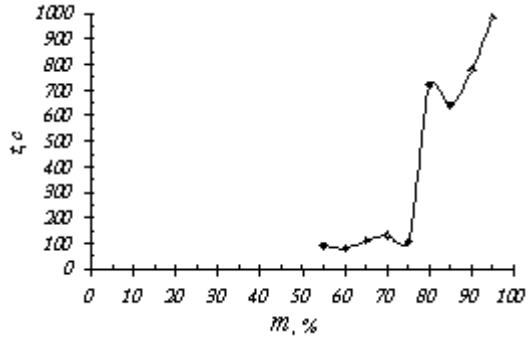

Figure 1. The time of the formation of a continuous luminescent zone along the whole laser-beam in aqueous–alcohol solutions of anthraquinone (at $C_A = 10^{-3}$ mole/liter) at various mass contents of alcohol *m* in the water–alcohol mixture

The influence of the structure of water–alcohol solutions is most clearly traced by the induction period of STS formation. From Figure 2 it is seen that the minimum induction period is observed only for solutions with a content of isopropanol from 30 to 70% of the total mass. At these concentrations the structure of the mixture is such that the "ice-like" structure of water under the action of the alcohol molecules embedded into it has not collapsed and alcohol microregions have not yet been formed. Such a solution contains three phases: alcohol, water, and a mixed region. Its structure is stronger than the structure of the solution containing 30% alcohol, i.e., the viscosity of solutions with a 30-70% alcohol concentration is higher than the viscosity of solutions with a content of alcohol less than 30 and more than 70%. Since the diffusion in a more viscous medium is slower than in a less viscous one, the reaction rate of quenching by dissolved oxygen of triplet states of anthraquinone decreases because of the slow penetration of oxygen molecules into the hydrophobic part of the micelle where anthraquinone molecules are concentrated as a result of its water insolubility [5].

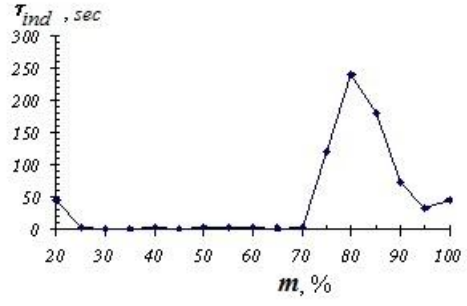

Figure 2. Induction period of the STS appearance in water–alcohol solutions of anthraquinone ($C_A = 10^{-4}$ mole/liter) at various mass contents of alcohol *m* in the water–alcohol mixture

Obviously, the formation of a luminescent zone along the whole laser-beam path during a short time and the decrease in the induction period of the appearance of an STS for these solutions are due to the fact that at these solvent ratios, besides water and alcohol, as mentioned above, there is a mixed phase. The alcohol radicals formed as a result of the interaction with an excited anthraquinone molecule can go out of the "cell" into the mixed phase [6], where they will act as "traps" for oxygen:

$$RCHOH^{\bullet} + O_2 \xrightarrow{k \approx 10^8 M^{-1} \cdot \sec^{-1}} RCH \begin{matrix} / \, OH \\ \backslash \, O - O^{\bullet} \end{matrix}$$

preventing the latter from penetrating into a micelle. The given circumstance will promote formation the ketyl radical as a result of the reaction of quenching by oxygen of triplet states of anthraquinone, participating in the reaction of formation of ketyl radical, becomes less possible.

The dependence of luminescence intensity solutions on the mass contents of alcohol in the aqueous–alcohol mixture isn't linear. It has been revealed that the luminescence intensity of the photoproduct formed under irradiation of a 30% alcoholic solution at the radiation maximum wavelength is lower by a factor of 2.3 than that of the photoproduct formed under irradiation of a water–alcohol mixture with a 70% content of alcohol. It would be expected that at a large quantity of alcohol, where the alcoholic regions grow in size and the probability of quenching the triplet states of anthraquinone by oxygen decreases, the luminescence intensity increases. However, the solubility of oxygen in alcohol (0.22 cm^3/cm^3) is higher than in water (0.03 cm^3/cm^3) [7] and, consequently, the more alcohol in the surroundings of the anthraquinone molecule, the more frequently it can encounter an oxygen molecule [8]. Therefore, the probability of quenching the triplet states of anthraquinone by oxygen:

$$^3A_1 + {}^3O_2 \rightarrow {}^1A_0 + {}^1O_2$$

increases so. Here $^1A_0$ and $^3A_1$ – the main condition and the triplet condition of the anthraquinone molecule respectively; $^1O_2$ and $^3O_2$ – the main condition and the triplet condition of the oxygen molecule respectively.

3. Conclusions

The microheterogeneous structure of water–alcohol solutions produces a strong effect on the intermolecular energy transfer rate, which in turn affects the behavior of luminescent STSs: a change in the induction period of the appearance of structures and their evolutionary development in space and time is observed. Such a behavior is associated with the micelle formation and solubilization processes proceeding in water–alcohol solutions The similarity to the STS evolution in alcoholic solutions showed up as the presence of the storage effect and a positive influence of local convective flows arising in the course of exothermal reactions on the STS formation. A considerable decrease in the induction period of the appearance of an STS (τ_{ind} < 1 sec) was registered under irradiation by UV light of solutions with a 70% mass content of alcohol in the matrix, which corresponds to a simplified structure of the alcohol–water mixture. The data obtained is in agreement with earlier developed concepts about structure of micellar solutions.

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